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Treatment of landfill gas with low methane content by biocover systems

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ABSTRACT

Landfills are significant sources of anthropogenic atmospheric methane (CH_4), which contributes to climate change. Large amounts of CH_4 are emitted from landfills in dilute form due to mixing with air in leachate collection systems, or during lateral migration away from landfills. The objective of this study was to investigate the CH_4 oxidation efficiency of a compost material subject to LFG diluted with atmospheric air resulting in CH_4 concentrations of 5–10% v/v. CH_4 oxidation rates and carbon dioxide (CO_2) production were measured through batch and dynamic column experiments where two laboratory scale biofilters were constructed. The columns were run at increasing flow rates. Column gas concentration profiles for each of five flow campaigns were compared to each other. This showed that oxygen (O_2) was present through the entire column and elevated CO_2 concentrations throughout the biofilters were found. Moreover, the oxidation process tended to be centred in the lower parts of both columns. It was observed that the biofilters performed better once they had adapted to the increasing loads of CH_4. In both columns, the maximum removal rate of CH_4 was found to be 98–100%. Using CH_4 mass balances the maximum oxidation rate was 238 g CH_4 m^{-2} d^{-1} in Column 1 and 483 g CH_4 m^{-2} d^{-1} in Column 2 (equal to the load). None of the biofilters reached their maximum CH_4 oxidation capacity, hence they could have been exposed to a larger CH_4 load. It was found that the retention time in the columns was not a factor limiting the oxidation process. High O_2 consumption and carbon mass balances underlined the strong microbial activity in the biofilters and it was not suspected that the methane oxidising bacteria were O_2 limited. The results of this study suggest that biofilters have great potential for reducing CH_4 in diluted LFG.

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1. Introduction

Landfills containing organic waste produce landfill gas (LFG) consisting of mainly methane (CH_4) and carbon dioxide (CO_2). Landfills are significant sources of anthropogenic atmospheric CH_4, which contributes to climate change (Bogner et al., 2008). At some landfills utilization of LFG is not or cannot be carried out, and the gas is either flared with risk of producing toxic combustion products or just emitted to atmosphere. As an alternative to mitigation by LFG collection and utilization systems, mitigation systems based on CH_4 oxidation processes may be implemented. Such systems, here called biocover systems are based on microbial CH_4 oxidation in full surface biological biocovers, biowindow systems or open or closed bed biofilter systems (Huber-Humer et al., 2008, Kjeldsen and Scheutz, 2014). The experiences so far have been on biocover systems, which mostly have been loaded with LFG typically containing about 40–45% v/v CO_2 and 55–60% v/v CH_4 (Scheutz et al., 2009). Several studies have shown that biocovers have a high potential for CH_4 oxidation resulting in high oxidation rates (Scheutz et al., 2009), however Scheutz and Kjeldsen (2003) reported that lack of oxygen (O_2) in the deeper part of a biocover/biofilter can be a limiting factor for the process of CH_4 oxidation.

For older landfills, the LFG concentration of CH_4 gradually decreases with time and an installed LFG utilization system may become uneconomical. At some landfills with relatively low CH_4 generation, the LFG may be significantly diluted with atmospheric air within or around the landfill. Many modern landfills receiving waste with a lower content of organic matter are not equipped with gas extraction systems. Studies have, however, revealed that significant quantities of LFG are produced at such landfills (Scheutz et al., 2011; Mønster et al., 2015), and that a significant part of the produced LFG is emitted through leachate collection wells and pumping stations as dilute LFG containing O_2 (Fredenslund et al., 2010). At old landfills, LFG often migrate laterally into surrounding residential areas. The risks from migrating LFG are often avoided by installation of wells at the perimeter of the landfill extracting pore gas containing low concentrations of

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CH_4 and high concentrations of O_2. The extracted pore gas is in most cases vented directly to the atmosphere (Kjeldsen, 1996).

The use of a biofilter for treating LFG (with a CH_4 concentration of about 30% v/v) by adding atmospheric air to the biofilter at three locations along the height of the biofilter was previous studied by Haubrichs and Widmann (2006). A similar study was made by Farrokhzadeh et al. (2017) also with air injection at up to three locations along the height of the filter. Both biofilters were closed to the atmosphere avoiding diffusion of O_2 from above. The experiments obtained high CH_4 removal efficiencies (88–100%), for the latter study up to 916 g CH_4 m^{-2} d^{-1}. Experiences with an open pilot scale biocover system at the AV Miljø Landfill receiving LFG with low CH_4 concentration (3–12% v/v) and elevated O_2 concentration (5–13% v/v) showed good performance (Cassini et al., 2017, Scheutz et al., 2017). The study at the AV Miljø Landfill showed that the presence of O_2 in the loaded LFG had a positive effect on the performance of the biocover. Due to a relatively low LFG load, the maximum methane oxidation capacity of the biocover system was not found (Scheutz et al., 2017). Information of a biocover system's CH_4 oxidation capacity is important for the design of the biocover system especially in respect to the necessary volume of the CH_4 oxidation layer. Hrad et al. (2012) studied the removal of CH_4 in open lysimeters containing a layer of waste underlying different types of top covers. The lysimeters were undergoing in situ aeration by injection of air into the waste layer through an injection well. Since the present CH_4 was formed by methanogenesis in the waste layer, the CH_4 loading to the top cover was not controlled nor measured. In summary, we conclude that no studies exist on the CH_4 oxidation capacity of open compost filters loaded with LFG diluted with atmospheric air.

The objective of this study was to investigate the potential methane oxidation efficiency of open biofilters treating landfill gas with low CH_4 contents and elevated contents of O_2. The objective was met by performance of laboratory column experiments simulating a biofilter consisting of compost and loaded with relatively high flows of diluted landfill gas (CH_4 contents of 5–10% v/v). Prior to the laboratory experiments, the compost material used in the biofilters was characterized in terms of moisture content, loss of ignition (LOI), bulk density as well as CH_4 oxidation potential and respiration potential.

2. Material and methods

2.1. Sampling and characterization of compost material

The compost used in this experiment was a yard-park compost collected from the recycling company, RGS 90, Copenhagen, Denmark. The compost was collected from a compost windrow containing about 18 months old matured compost. About 60 kg (wet) compost was sampled and homogenized by mixing the whole sample on a tarpaulin. To lower the initial water content the compost was dried for three days at room temperature. The characterization of the compost was done based on the following parameters; moisture content, loss on ignition (LOI) and bulk density. The moisture content and LOI were determined gravimetrically by weight loss after 24 h at 105 °C and weight loss after 3 h at 550 °C, respectively.

The bulk density; ρ_b (dry weight) was determined based on weight measurements of the compost. The compost was packed in an 1800 mL cylinder and weighed. The compost was packed in the cylinder by hand applying a light pressure to settle the compost. The same technique as was used to pack the experimental columns. To avoid layering of the compost material, the top 1 cm was carefully loosen and mixed before the next 3–4 cm layer was filled in. The gas-filled porosity and the total porosity were determined based on the measured bulk density of the compost and an estimate of the particle density; ρ_d of 2.02 kg L^{-1} (for fine compost) from Pedersen et al. (2011). The following equations were used for determining bulk density, total porosity, water-filled porosity and gas-filled porosity:

$$\rho_b = \frac{M_{c,w}}{V_c \cdot (1 + MC)}$$

where ρ_b is bulk density (kg dry compost L^{-1} dry compost sample), $M_{c,w}$ is weight (kg) of wet compost sample, V_c is volume (L) of compost sample and MC is gravimetric water content (kg water kg^{-1} dry compost).

$$\varepsilon_t = 1 - \frac{\rho_b}{\rho_d}$$

where ε_t is total porosity of packed compost (L void space L^{-1} packed dry compost) and ρ_d is particle density of compost material (kg L^{-1} compost dry solid).

$$\varepsilon_w = \frac{MC \cdot \rho_b}{\rho_w}$$

where ε_w is water-filled porosity (L water L^{-1} packed dry compost) and ρ_w is density of water (kg water L^{-1} water).

$$\varepsilon_a = \varepsilon_t - \varepsilon_w$$

where ε_a is gas-filled porosity (L gas L^{-1} packed compost).

2.2. Batch incubation experiments determining CH_4 oxidation potential and respiration

To ensure that the compost had potential of methane oxidation, batch incubations were performed to determine the potential CH_4 oxidation rates and respiration rates. The batch experiments were carried out by adding 100 g of moist compost into 500 mL incubation glass bottles. The incubation bottles were sealed with gastight butyl rubber septa (17 mm thick) (Norsorex DC 97 rubber stoppers) and aluminium screw caps, 200 mL of air was withdrawn with a hypodermic needle and syringe, replaced with 120 mL O_2 and 80 mL CH_4. This gave an initial concentration of 35–36% v/v O_2, 15–16% v/v CH_4 and approximately 50% v/v N_2. Bottles intended for CH_4 oxidation capacity evaluation were pre-treated overnight using this method to activate methanotrophic bacteria naturally present in the compost. This normally reduces lag phases and thus maximal CH_4 oxidation rates can be calculated using the initial CH_4 concentration and time. Bottles were re-opened after pre-treatment, and flushed with air for 15 min to remove remaining CH_4 and CO_2, resealed and again 200 mL air was extracted to be replaced with 120 mL O_2 and 80 mL CH_4. After all the O_2 was used, the experiments were stopped and the incubation bottles were re-spiked with O_2 and CH_4 in the same volumes. Subsequently, samples were taken at regular intervals. The initial high O_2 content should assure sufficient O_2 for both CH_4 oxidation and compost respiration. All incubation experiments were done in duplicates at room temperature (approximately 21–22 °C) and with two empty control bottles run in parallel. The CH_4 oxidation test was run for about 50 h. Gas samples were taken at regular intervals (approximately every 3 h, except at night time) from the incubation bottles and transferred to standard vacuum 5 mL Exetainers© (Vial 819 W, 6 mL, Labco Ltd., UK) by using gas tight syringes. Gas samples composition (O_2, CO_2 and CH_4 concentrations) were analysed by using a gas chromatograph (confer Section 2.5).

The respiration of the compost was determined using the same method as for the CH_4 oxidation potential batch experiments, however after withdrawing 200 mL of air only O_2 was supplied (120 mL). Gas samples were taken at regular intervals during the test period of about 100 h.

2.3. Column experiments – design and set-up

Column experiments were setup to simulate an open biofilter receiving a dilute stream of LFG. Three rigid PVC columns (h = 100 cm; i.d. = 20 cm) were used to examine the CH_4 oxidation process; one control and two experimental columns (Fig. 1). Both ends of the PVC columns were closed with PVC end caps, which were fitted with rubber O-rings to ensure a gas-tight fit. The bottom cap had one inlet while the top cap had both an inlet and an outlet. The control column was packed with gravel with 2.00–3.55 mm grain size (size 6 from DanSand, Brædstrup, Denmark) whereas the active columns were packed with compost in a total height of 87 cm leaving a high headspace on top of the compost column of about 10 cm. The column headspace was fed with a constant ambient air flow of in average 109 mL min^{-1} using a vacuum pump (type N 86 KN.18, KNF Neuberger, Germany), which was calibrated prior and during the run of the experiment. The air flow was continuously monitored by a ball flow meter (Key Instruments, Model no. FR2A12BUBN). Prior to each sampling campaign, the flow out of the headspace was measured by fitting a soap bubble flow meter (Producer unknown; length 30 cm, inner diameter 1.5 cm) to the outlet tubing. The air standing in the headspace was replaced to simulate an open biofilter with atmospheric conditions in the headspace and thus supplying O_2 by vertical diffusion into the compost material. A 3 cm gravel layer (Size 6 from DanSand) was distributed in the bottom on top of a perforated nylon net to ensure a homogeneous gas distribution in the bottom. Larger twigs and stones had been removed from the compost mix prior to the experiment, and lumps of compost had been sieved through a 5.40 mm mesh to avoid inhomogeneities. The compost was then packed on top of the gravel layer. Sampling ports were placed alongside the column length with 5 cm between each port and the bottom port being located 5 cm from the bottom inlet.

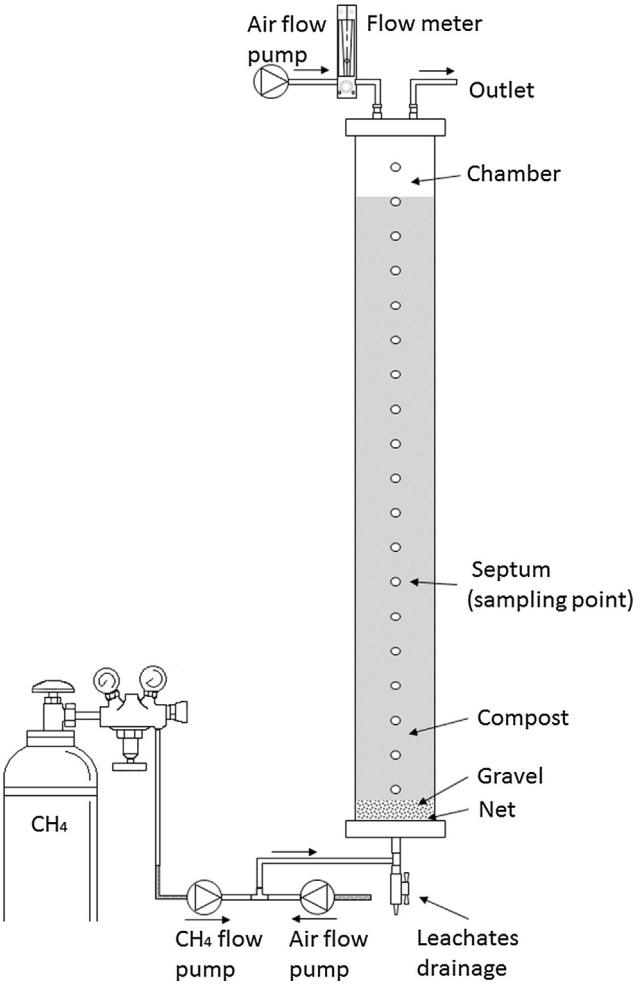

Fig. 1. Conceptual setup of the dynamic column.

A flow of CH_4 (99.5% v/v. pure CH_4, AGA, Sweden) mixed with atmospheric air was fed into the bottom using two peristaltic pumps (BT100-2J, Longer Precision Pump Co., Ltd., China) equipped with YZ II 15 (Longer Precision Pump Co., Ltd., China) pumping heads for each columns. Tygon® norprene pump tubes (Saint-Gobain Performance Plastics, France) with an inner diameter of 1.6 mm (CH_4) and 4.8 mm (atmospheric air) were used. The pump tubes were re-placed regularly to avoid time changes in flow rates. Prior to each sampling campaign, the CH_4 inlet flow to each column was measured by injecting a small amount of water using a syringe into the tube connected to the pumps. The time it took the water to travel 10.0 cm was recorded and knowing the inner dimension of the tube the flow was calculated.

Gas samples (5.0 mL) were taken in every second sampling port, starting at the bottom, and transferred into evacuated glass vials (Exetainer® vials (Labco Limited, United Kingdom)). Water produced in the column during the experiment leached to the bottom of the column. The water was occasionally drained away through a valve at the bottom of the column (typically once every third day) (Fig. 1). The column experiment was carried out at room temperature (approximately 20–22 °C).

In interpretations of the results, the gas retention time; T_a; in the column was used. This parameter was calculated using the following equation:

$$T_a = \frac{\varepsilon_a \cdot V_{column}}{Q_{gas}}$$

where T_a is the gas retention time in the compost column (hour), ε_a is gas-filled porosity (L gas L^{-1} packed compost), V_{column} is the volume (L packed compost) of the compost column, and Q_{gas} is the total flow of gas (atmospheric air + CH_4) (L gas h^{-1}).

2.4. Column experiments – experimental run

Table 1 shows an overview of the CH_4 and air inlet flows to the columns, together with gas retention times and column CH_4 loads. In order to study the methane oxidation capacity of biofilters at different CH_4 loadings, the column experiments were run with five different inlet flows ranging from 5 to 150 mL min^{-1} (total inlet flow) and two different inlet CH_4 concentrations (5 or 10% v/v) (Table 1). The experiment was divided into five measuring campaigns each of 14 days and with increasing CH_4 loadings to the columns. The CH_4 inlet concentration to Column 1 was 5% v/v throughout the experiment period. The inlet flow was however increased in five steps (5, 25, 50, 75, and 150 mL min^{-1}) resulting in CH_4 loading rates of 8, 38, 76, 115, and 229 g CH_4 m^{-2} d^{-1}, respectively. During the first three campaigns, Column 2 was run in the same way as Column 1 (CH_4 inlet concentrations of 5% v/v and inlet flows of 50, 75, and 150 mL min^{-1}) functioning as a duplicate to Column 1. However during the following two campaigns, the CH_4 inlet concentration to Column 2 was increased to 10% v/v and the inlet flow was changed to 75 and 150 mL/min resulting in CH_4 loadings of 229 and 458 g CH_4 m^{-2} d^{-1}, respectively. The Control column was run in the same way as Column 1.

During each campaign, gas samples were taken (inlet, outlet and sampling ports) five times during the 14 day period. After changing the flow, the columns were left three days to stabilize and assure a homogeneous gas distribution throughout the columns before the first samples were taken. CH_4 oxidation rates

Table 1
Overview of the column set-up showing planned bottom inlet flows, CH_4 loadings, retention times, etc.

Column no.	CH_4 inlet conc. [% v/v]	Total inlet flow [mL min^{-1}]	CH_4 inlet flow [mL min^{-1}]	Air inlet flow [mL min^{-1}]	Total inlet flux [m^3 m^{-2} d^{-1}]	CH_4 inlet flux [m^3 CH_4 m^{-2} d^{-1}]	Air inlet flux [m^3 air m^{-2} d^{-1}]	Retention time[a] [h]	CH_4 load [g CH_4 m^{-2} d^{-1}]
Control + 1 + 2	5	5	0.25	4.75	0.229	0.0115	0.218	36.7	7.64
Control + 1 + 2		25	1.25	23.8	1.15	0.0573	1.09	7.3	38.2
Control + 1 + 2		50	2.50	47.5	2.29	0.115	2.18	3.7	76.4
Control + 1		75	3.75	71.3	3.44	0.172	3.27	2.4	115
Control + 1		150	7.50	143.0	6.88	0.344	6.53	1.2	229
2	10	75	7.50	67.5	3.44	0.344	3.09	2.4	229
2		150	15.0	135.0	6.88	0.688	6.19	1.8	458

[a] The calculated retention time is based on a gas-filled porosity of 0.35.

(g m^{-2} d^{-1}) and CH_4 oxidation efficiencies (%) were calculated by establishment of the CH_4 mass balance for the system, i.e. the CH_4 mass flow out of the system subtracted from the mass flows into the system. Similar carbon mass balances were established considering CH_4 and CO_2 inlet and outlet mass flows.

2.5. Gas analysis

The 5 mL gas samples taken from the incubation and column experiments were analysed for contents of CH_4, O_2, CO_2 and N_2 using gas chromatography on a 490 Micro GC (Agilent Technologies, USA). The Micro GC was able to separate the gases under isothermal conditions. The CH_4 and CO_2 were separated on a 10 m Q-PLOT capillary column (Agilent Technologies, USA) at 80 °C and with a sample injection time of 100 ms at an injection temperature of 110 °C. The O_2 and N_2 were separated on a 20 m Molsieve 5A capillary column (Agilent Technologies, USA) at 62 °C. The carrier gas of the Micro GC was helium and the gas standards used for calibration ranged from 0.1 to 10 % v/v CH_4 and CO_2 and 0.1–5% v/v O_2, with N_2 as balance gas.

3. Results and discussion

3.1. Compost material characteristics

The compost was analysed for different parameters and the results are shown in Table 2. The gravimetric water content was found to be 56.3% dry matter (DM), while the water content based on the wet weight of the compost was 36.0% w/w (wet weight). The organic matter content was 24.4% of DM, which is in line with the recommended level of >15% of DM (Huber-Humer et al., 2009). The bulk density of the compost as packed in the columns was 0.55 kg L^{-1}, which is less than the 0.8–1.1 kg L^{-1} proposed as the optimal range (Huber-Humer et al., 2009). The gas-filled porosity (0.40) and the total porosity (0.73) of the compost as packed in the columns were comparable to the two compost porosities of 0.37/0.75 and 0.45/0.80 (gas-filled/total) reported by Pedersen et al. (2011). The gas-filled porosity was above the proposed value of >0.25 recommended by Huber-Humer et al. (2009).

Table 2
Compost characteristics.

Parameter	Value
Gravimetric water content [% DM]	56.3
Water content [%][a]	36.0
Organic matter content [% DM]	24.4
Bulk density [kg DM L^{-1}]	0.553
Total Porosity [–][b]	0.726
Air-filled porosity [–][b]	0.399

[a] Water content based on wet weight of compost.
[b] Based on estimated particle density of 2.02 kg/L for similar compost type used by Pedersen et al. (2011).

3.2. Batch experiments – compost CH_4 oxidation potential and respiration

Table 3 shows the results from the CH_4 oxidation potential experiments. Fig. 2 shows a representative example of the concentrations of CH_4, CO_2 and O_2 as a function of time for a methane oxidation (A) and a respiration (B) incubation batch. The CH_4 oxidation rates ranged from 32.2 to 33.8 μg CH_4 $gDW^{-1}h^{-1}$. Respiking the containers with CH_4 and O_2 resulted in slightly lower CH_4 oxidation rates (between 19.4 and 32.2 μg CH_4 $gDW^{-1}h^{-1}$), which was unexpected as the rate usually increases after respiking (Pedersen et al., 2011). It was not possible to find the reason to the decrease.

The compost stability was tested in respiration experiments measuring the O_2 consumption rate and the results are shown in Table 3. The O_2 consumption in the batch experiment for 100 g compost resulted in an average respiration rate of 20.9 μg O_2 $gDW^{-1}h^{-1}$. This value is well below the recommended maximum respiration rate of <48 μg O_2 $gDW^{-1}h^{-1}$, (calculated from <8 mg O_2 gDW^{-1}) recommended by Humer and Lechner (2001). The O_2 consumption in the respiration test made up about 20% of the total O_2 consumption measured in the CH_4 incubation tests, which was about 98 μg O_2 $gDW^{-1}h^{-1}$ indicating a reasonable low competition for O_2 between the two processes, as desired.

Overall, the results from the batch incubation experiments showed that the yard-park compost from RGS 90 had chemical and physical properties suitable to support methanotrophic microorganisms, and thus was a suitable material for the construction of a dynamic column biofilter setup.

3.3. Column test – gas concentration profiles

Figs. 3–5 illustrate a selection of the gas concentration profiles of CH_4, CO_2 and O_2 in the column experiments. All obtained gas concentration profiles can be seen in Supporting Information (SI). The N_2 gas concentration profiles were relatively constant throughout the columns and close to 80% v/v as N_2 diffuses in from the ambient air flow in the top chamber and also is present in sub-

Table 3
CH_4 oxidation potential and respiration test results from batch incubation experiments containing 100 g compost material. CH_4, CO_2, and O_2 rates are presented as ranges based on the two values obtained from the duplicates, and with the average value shown in parenthesis.

Test	CH_4 oxidation incubations		Respiration test
	First test	Respike	First test
CH_4 rate [μg CH_4 $gDW^{-1}h^{-1}$]	32.2–33.8 (33.0)	19.4–32.2 (25.8)	–
O_2 rate [μg O_2 $gDW^{-1}h^{-1}$]	97.9–98.8 (98.3)	67–97.9 (82.6)	20.2–21.7 (20.9)
CO_2 rate [μg CO_2 $gDW^{-1}h^{-1}$]	29.2–31.1 (30.2)	28.0–31.1 (29.5)	22.3–27.5 (24.9)

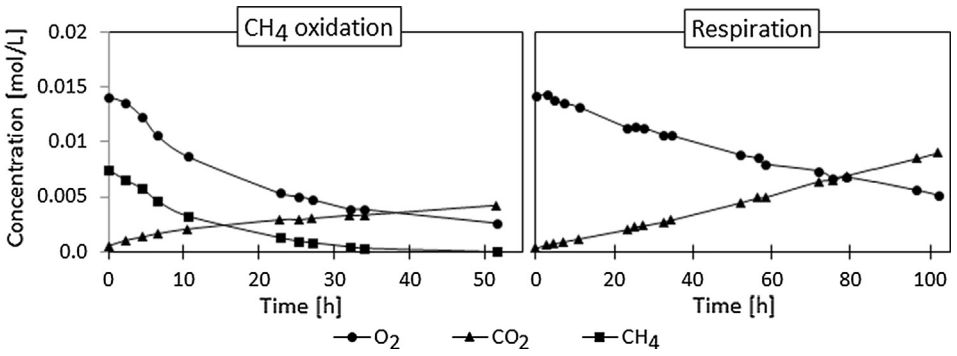

Fig. 2. Headspace concentration of gas components (CH_4, CO_2, and O_2) in a compost (100 g wet compost) incubation batch experiment as function of time. Result from the CH_4 oxidation test (left) and Respiration test (right) are given.

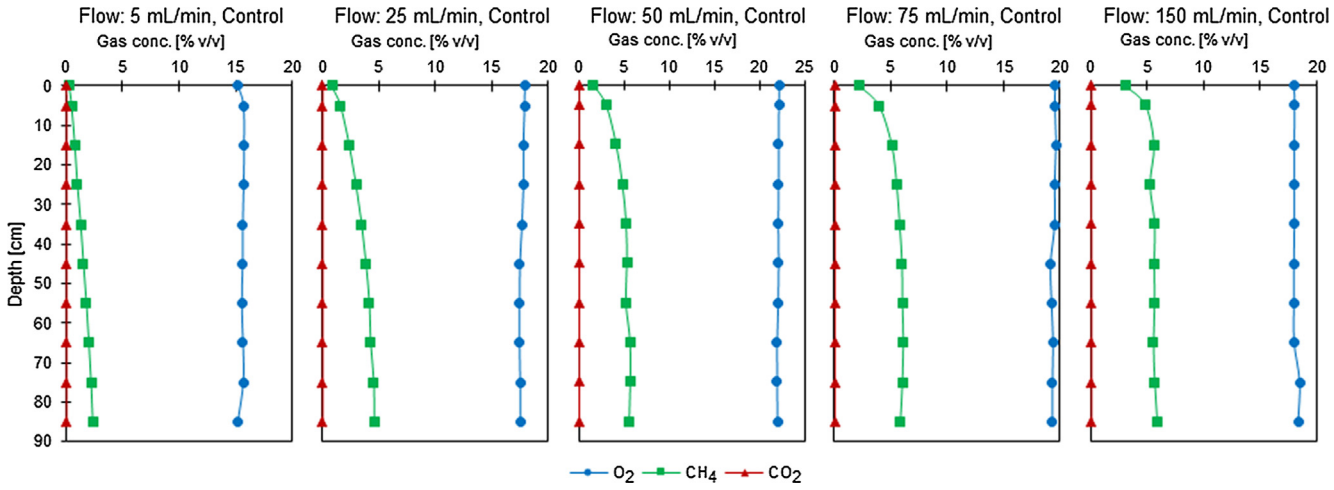

Fig. 3. Gas concentration profiles for the Control Column with 5% CH_4 (v/v) inlet flow concentration for day 7 of each of the five flow campaigns (5 mL min^{-1} flow, 25 mL min^{-1} flow, 50 mL min^{-1} flow, 75 mL min^{-1} flow and 150 mL min^{-1} flow.

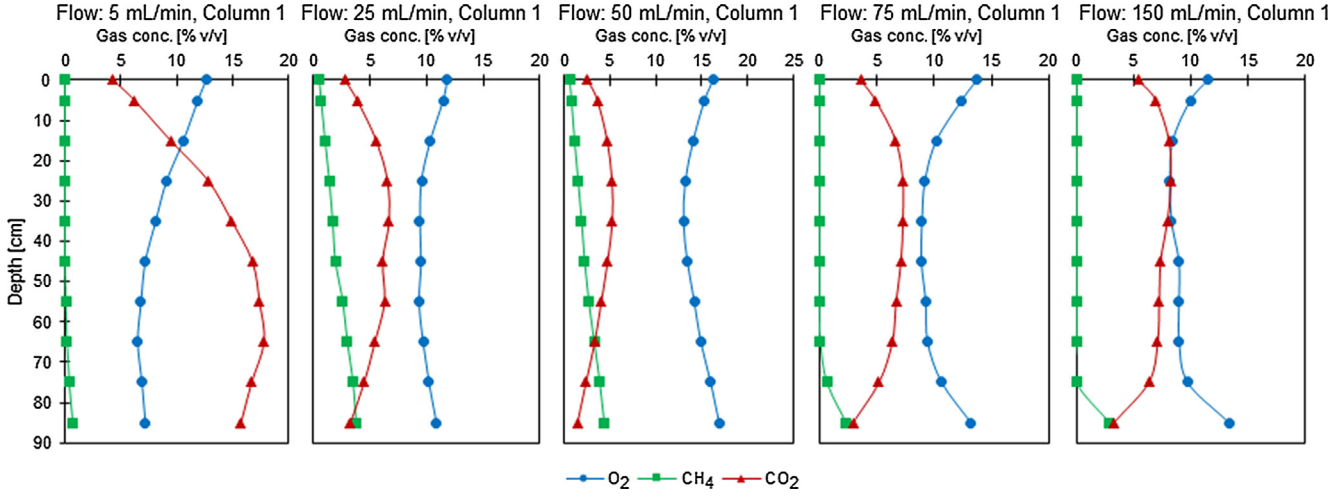

Fig. 4. Gas concentration profiles for Column 1 with 5% CH_4 (v/v) inlet flow concentration measured at day 14 of each of the five flow campaigns (5 mL min^{-1} flow, 25 mL min^{-1} flow, 50 mL min^{-1} flow, 75 mL min^{-1} flow and 150 mL min^{-1} flow).

stantial volumes in the inlet gas fed to the bottom of the column. N_2 concentration profiles were thus left out of the figures. In the control column, containing gravel, the CO_2 and O_2 levels were constant (<1% v/v and 16–21% v/v, respectively), while the CH_4 level decreased from about 3–5% v/v in the first sampling port in bottom of the column and to less than < 1% v/v in the outlet at the top of

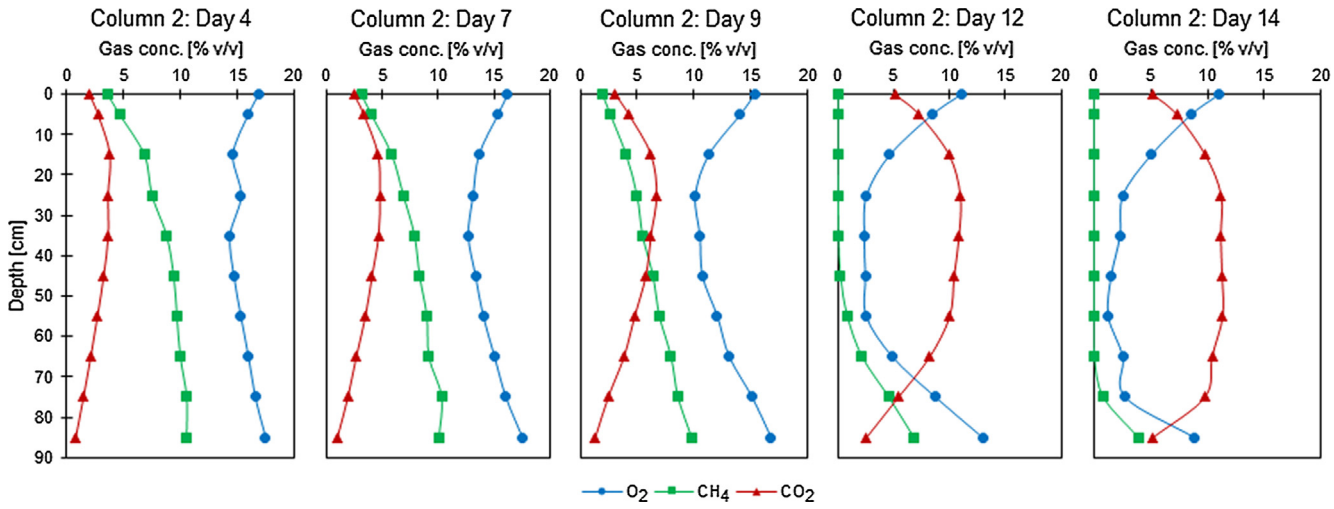

Fig. 5. Gas concentration profiles for Column 2 during the 75 mL min^{-1} flow campaign and 10% CH_4 (v/v) inlet flow concentration for different days during the campaign; day 4, day 7, day 9, day 12 and day 14).

the column (Fig. 3). This indicates that the CH_4 profile is governed by a combination of advection (making the profile vertical in the lower part) and diffusion (dragging the profile in the upper part towards the low value in the headspace).

Fig. 4 presents a collection of gas concentration profiles for Column 1 obtained on the last day of each flow campaign. During the first campaign, all the CH_4 was oxidised already in the lowest part of the column and the highest concentration of CO_2 was detected (17.8% v/v) during this campaign. However, it is most likely that some of this CO_2 could be from the compost respiration rather than from the CH_4 oxidation process. During the two next flow campaigns (inlet flows of 25 and 50 mL min^{-1}), CH_4 was present in all depths of the column, and it was seen that the concentrations of CO_2 was lower during these two flow campaigns. No time-dependent variation in the profiles during the 25 mL min^{-1} flow campaign were observed (see SI), which indicates that the column reached steady state, obtaining a maximum oxidation efficiency for this flow condition. However, the last two sub-figures in Fig. 4 from day 14 for the 75 and 150 mL min^{-1} flow campaigns show that the column was able to completely oxidise CH_4 locally in the bottom part of the column, the lowest 25 cm and 15 cm, respectively. This indicates that the bacterial population in the column, during the first inlet flow campaigns (1–3) had an adaption period and was thereafter capable of completely oxidising the higher CH_4 loads.

Fig. 5 presents the five measured gas concentration profiles (day 4, 7, 9, 12 and 14) from the 75 mL min^{-1} flow campaign for Column 2. These profiles are very different from what was found in Column 1, probably as a result of the higher CH_4 loading concentration. The figure shows a significant development of the shape of the gas concentration profiles through the 14 day duration of the flow campaign. The gas concentration profiles show gradually higher oxidation capacity indicating a development of the methanotrophic population. This is seen by the decrease in CH_4 and O_2 concentrations and an increase in the CO_2 concentrations. CH_4 is detected throughout the entire column in the beginning of the campaign (day 4); decreasing from the bottom of the column to the top with a starting point around 4–5% CH_4 (v/v). As the inlet flow is kept constant during the 14 days, the CH_4 is more efficiently oxidised in the bottom of the column and thus leaving less gas to penetrate the remaining upper part of the column. Furthermore, the figure reveals that the biofilter could have been exposed to a greater mass of CH_4 in the inlet flow as it is able to completely oxidise CH_4. The development of the O_2 consumption is also interesting in these profiles. The additional O_2 supply in the bottom of the column seems to have a positive effect on the oxidation process as the microbial population does not become limited by O_2 in the deep part of the column, which has been seen in other compost column studies (Scheutz et al., 2009).

The lowest O_2 concentration measured of 0.40% v/v was found during the 150 mL min^{-1} flow campaign in Column 2. Gebert et al. (2003) found that the CH_4 oxidation process became limited if the O_2 concentration was lower than the range of 1.7–2.6 % v/v. However, this low O_2 concentration was only measured in a depth of 55 cm, i.e. <10 cm of the column was subject to this low O_2 concentration. As the CH_4 was already oxidised prior to this depth, O_2 was not considered as a limiting factor for CH_4 oxidation.

3.4. Methane oxidation rates and efficiencies

Table 4 provides an overview of the column results showing column CH_4 loads (g CH_4 m^{-2} d^{-1}), CH_4 oxidation rates (g CH_4 m^{-2} d^{-1}), CH_4 oxidation efficiencies (%) and carbon mass balances given as averages of each inlet flow campaign. The control column showed closed CH_4 and carbon mass balances (in most cases <±10% deviation) indicating a gas tight system with no microbial activities. The observed deviation was due to uncertainty associated with variations in inlet and outlet flows, flow measurements, gas sampling and analysis and is considered acceptable for an experimental study of this kind.

Very high CH_4 oxidation efficiencies of up to 100% were obtained in Column 1 during the 5, 75 and 150 mL min^{-1} flow campaigns (Campaign 1, 4, and 5). Hence, during these inlet flow campaigns also the oxidation rates were high with a CH_4 maximum rate of 238 g CH_4 m^{-2} d^{-1} during the 150 mL min^{-1} inlet flow, equalling the inlet CH_4 load (Table 4). Furthermore, these results indicate the possibility that the biofilter could have handled much higher CH_4 loads. The lower oxidation efficiencies (about 50%) during the 25 and 50 mL min^{-1} inlet flow campaigns (Campaign 2 and 3), however, indicates that the methanotrophic bacteria needed time to grow and adapt to the CH_4 loads, which was also supported by the column gas concentration profiles (Table 4). Pedersen et al. (2011) also observed an increase in the oxidation activity during the first 30–40 days of column operation reaching a maximum oxidation rate around day 40. In a column experiment containing a 1:1 mix of landfill soil and compost and fed with a CH_4 load of 802 g m^{-2} d^{-1}, Amodeo et al. (2015) obtained a CH_4

Table 4
Overview of column results showing average input CH_4 loads, CH_4 oxidation results and carbon mass balances during the five inlet flow campaigns in the three columns.

Column	Campaign	Measured inlet flow [mL min^{-1}]	Retention time [h]	Initial conc. [% CH_4]	CH_4 load [g CH_4 m^{-2} d^{-1}]	CH_4 oxidation efficiency [%]	CH_4 oxidation rate [g m^{-2} d^{-1}]	$Carbon_{in}$ [g m^{-2} d^{-1}]		$Carbon_{out}$ [g m^{-2} d^{-1}]	
								C-CH_4	C-CO_2	C-CH_4	C-CO_2
Control	1	6.06	30.0	4.96	9.20	1.61	0.148	6.89	0.789	6.77	1.91
	2	24.1	7.53	4.92	36.2	−2.06	−0.731	27.1	0.907	27.7	1.85
	3	51.1	3.56	4.84	75.5	−11.3	−8.50	56.5	1.08	62.9	2.19
	4	75.5	2.41	4.79	110	−7.34	−8.16	82.7	1.24	88.8	2.41
	5	149	1.22	4.96	226	−12.0	−27.3	169	1.72	189	3.33
Column 1	1	6.03	30.1	4.44	8.19	100	8.19	6.13	0.777	0.00	41.0
	2	24.8	7.33	4.96	37.5	51.6	19.3	28.1	0.899	13.6	55.7
	3	49.7	3.65	5.01	76.1	47.9	36.3	57.0	1.06	29.8	64.8
	4	75.5	2.40	4.88	113	94.4	107	84.4	1.23	4.68	104
	5	150	1.21	5.21	238	100	238	178	1.71	0.00	216
Column 2*	3	49.7	3.66	5.10	77.5	30.4	23.5	58.0	1.06	40.4	59.6
	4	74.7	2.43	9.57	218	63.1	137	164	1.20	60.7	114
	5	151	1.20	10.6	488	99.0	483	365	1.67	3.83	292

* For Column 2 only results from Campaign 3 to 5 are shown due to a leakage during Campaign 1 and 2.

removal efficiency of around 35% (corresponding to an oxidation rate of 280 g m^{-2} d^{-1}, which is comparable to the maximum oxidation rate obtained for Column 1 in our study). The lower CH_4 oxidation efficiency obtained by Amodeo et al. (2015) was most likely due to a low CH_4 retention time of just 9.5 min, approximately.

The Column 2 results from the 50 mL min^{-1} flow campaign (Campaign 3) were slightly different from what was found for the Column 1 50 mL min^{-1} flow campaign. In Column 2, an average oxidation efficiency of 30% and an average oxidation rate of 24 g CH_4 m^{-2} d^{-1} were observed. During Campaign 3, the two columns were identical in their setup. However, lower oxidation efficiencies and oxidation rates were expected for Column 2, as this was not exposed to the same load in the previous two flow campaigns due to a CH_4 leakage in Column 2 resulting in a lower loading in comparison to Column 1. However, during Campaign 4 where the inlet flow to Column 2 was increased to 75 mL min^{-1} and the inlet CH_4 concentration was increased to 10% v/v, the average oxidation efficiency increased to 63% and the oxidation rate to 137 g CH_4 m^{-2} d^{-1} suggesting that the growth of the methanotrophic bacteria increased rapidly. A further increase in the inlet flow to 150 mL/min (corresponding to a CH_4 load of 488 g CH_4 m^{-2} d^{-1}) (Campaign 5) resulted in a CH_4 oxidation efficiency of 99%. As for Column 1, these results show that Column 2 most likely did not reach its maximum CH_4 oxidation capacity and thus most likely could have handled even higher CH_4 loads. The CH_4 oxidation rates obtained for these two biofilters are comparable to the potential CH_4 oxidation rate of 300 g CH_4 m^{-2} d^{-1} reported by Scheutz et al. (2017), who estimated this value based on laboratory and field investigations from a large scale biocover (AV Miljø biocover in Denmark). This study thus supports the results from the study at the AV Miljø landfill where high CH_4 oxidation rates of a large scale biofilter were obtained when the biofilter was loaded with dilute LFG containing significant concentrations of O_2.

The average retention time for the columns ranged from about 30 to 1.2 h (Table 4). Even at the lowest retention time (1.2 h), the columns were able to completely oxidise the fed CH_4 resulting in average CH_4 oxidation rates of 238 and 483 g CH_4 m^{-2} d^{-1} (Column 1 and 2, respectively) and CH_4 oxidation efficiencies of almost 100%. These results do not indicate that the CH_4 oxidation process was limited by too short retention times in the columns as high removal rates were measured, a tendency, which was also reported by Dever et al. (2011). However, other previous studies using diluted LFG, as e.g. Amodeo et al. (2015), Rose et al. (2012) and Girad et al. (2011) treated with low retention times (maximum 9 min) did not find as high oxidation efficiencies as in our experiment, suggesting that there is a minimum limit for when the retention time affects the CH_4 oxidation efficiency and thus the oxidation rates.

3.5. Carbon mass balance

Fig. 6 illustrates the carbon mass balances based on CH_4 and CO_2 column mass inlet and outlet flows as presented in Table 4. During Campaign 1, 2 and partly Campaign 3 for Column 1, the carbon outlet flow consisting of mainly CO_2 surpassed the carbon inlet flow consisting of mainly CH_4 (this is also the case for most of Campaign 3 for Column 2). Two processes are contributing to CO_2 generation in the column. The methanothrophic oxidation reaction generates CO_2 – theoretically one mole of CO_2 per mole CH_4 oxidised (Hanson and Hanson, 1996). However, in reality less than one mole of CO_2 is generated per mole of CH_4 oxidised due to assimilation of carbon into microbial biomass (Hilger and Humer, 2003). Second, the respiration of compost generates CO_2 as also observed in the batch incubation experiments. The higher molar CO_2-C outlet flow in comparison to the molar CH_4-C inlet flow is due to respiration activity in the columns, especially at relatively low CH_4 loads where this becomes the dominating process in CO_2 generation. Based on the results from Column 1 – Campaign 1 (fed with about 0.5 mol CH_4 m^{-2} d^{-1}), the CO_2-C from compost respiration can be estimated to be around 2.8 mol CO_2 m^{-2} d^{-1} (assuming that CH_4 is oxidised to CO_2 in a 1:1 ratio), which could be expected to be relatively constant throughout the experiment and unaffected by increasing CH_4 loads as long as the compost material in the columns does not become O_2 limited. At high CH_4 loads (as seen in Column 1 and Column 2 – Campaign 4 and 5) a higher share of the carbon in the generated CO_2 will come from oxidised CH_4. The molar ratio of CH_4 to CO_2 being less than one, due to carbon assimilation into biomass and the CO_2 generated by compost respiration being constant, result in a lower molar CO_2-C outlet flow in comparison to the CH_4-C inlet flow as observed in Column 1 and Column 2 – Campaign 4 and 5. Assuming a constant CO_2 generation rate of 2.8 mol CO_2 m^{-2} d^{-1} from compost respiration, the carbon uptake by the methanotrophic bacteria can be estimated to between 30 and 60% of the carbon fed as CH_4. This is comparable to earlier incubation tests, which showed a carbon uptake of approximately 48% of the carbon (background soil respiration subtracted) for methanotrophic biomass growth (Scheutz et al., 2004). Börjesson et al. (1998), found CO_2 to CH_4 ratios between 0.17 and 0.36 indicating that between 64 and 83% was assimilated, while Kightley et al. (1995) found that 69% of oxidized methane was assimilated into biomass in soil cores.

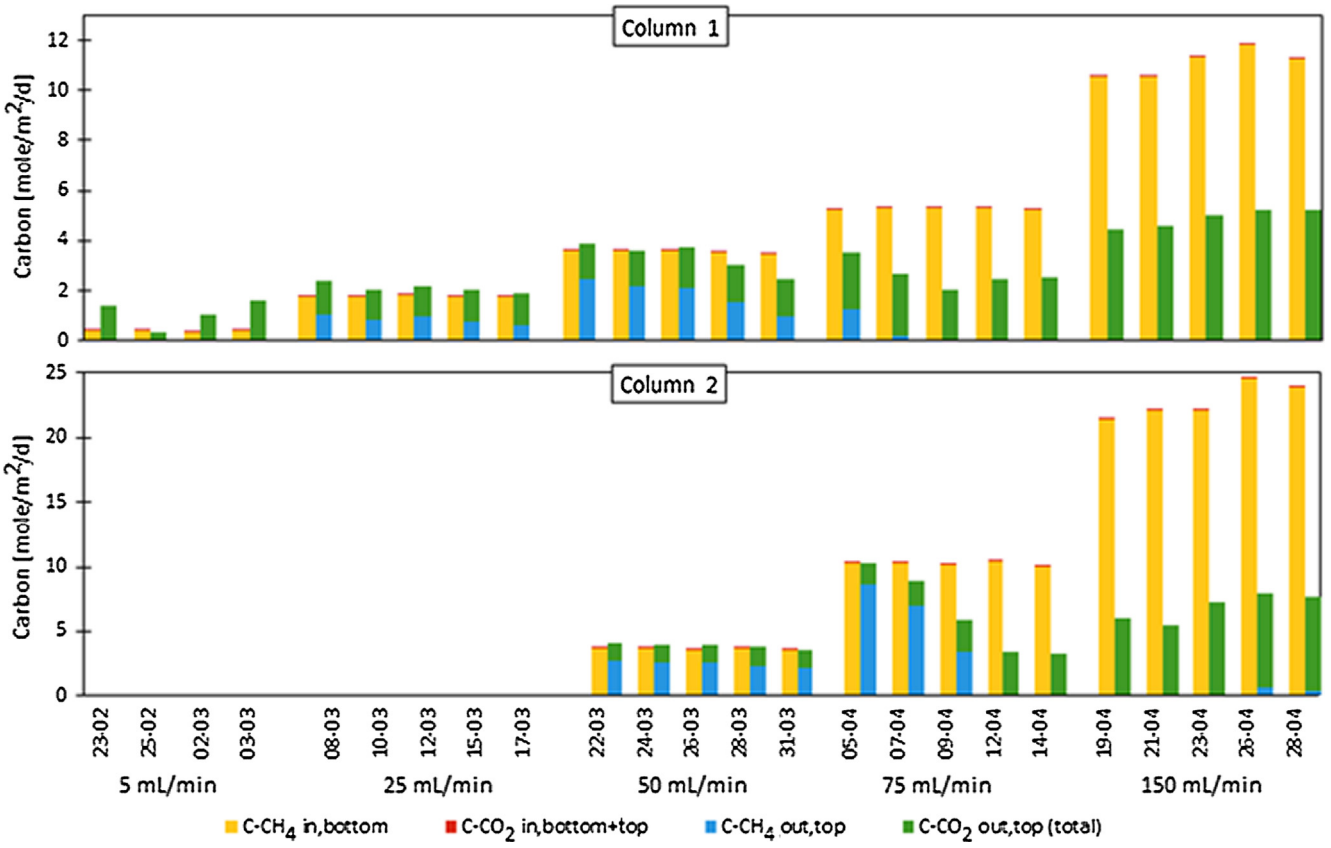

Fig. 6. Carbon mass balance between load and outflow of CH_4 and CO_2 in Column 1 and Column 2. First two flow campaigns for Column 2 are neglected in this figure due to leakage.

4. Conclusion

Laboratory columns simulating a biofilter fed at the bottom with diluted LFG and open to the atmosphere at the top were constructed and supplied with five different CH_4 inlet flows (5–150 mL min^{-1}) containing 5 or 10% CH_4 (v/v). Column gas concentration profiles suggested high methanotrophic activity in the lower parts of the columns. At all tested column inlet flow rates and CH_4 loads, O_2 was present in the pore gas through the entire column, and hence O_2 was not a limiting factor for the oxidation process during the experiment. During the run of the experiment, the microbial population adapted to CH_4 oxidation during the initial test campaign with lower CH_4 inlet flows and were able to completely oxidise the fed CH_4 during the highest inlet flows. The highest CH_4 oxidation rate found was 438 g CH_4 m^{-2} d^{-1}, however at this CH_4 load, the fed CH_4 was completely oxidized indicating that the maximum oxidation capacity of the column had not been reached. The highest CH_4 oxidation rate was obtained at the lowest retention time (1.2 h) and thus lowering the retention (from 36.7 to 1.2 h) did not seem to limit the oxidation capacity of the simulated biofilters under the tested conditions. This was most likely a result of a sufficient oxygen supply and a well-adapted microbial population. Compost respiration in the column resulted in a CO_2 generation of about 2.8 mol CO_2 m^{-2} d^{-1}. In conclusion, this study showed that biofilters supporting methanotrophic bacteria have a potential for treating diluted landfill gas with low CH_4 and high O_2 concentrations at relatively high flow rates and low retention times. Future studies should involve long term pilot scale tests fed with diluted landfill gas mixtures.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2018.11.011.

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